

Empirical InfraRed Line Lists for Five SO₂ Isotopologues: ^{32/33/34/36}S¹⁶O₂ and ³²S¹⁸O₂

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Abstract

Using the latest published, empirically refined potential energy surface (PES) Ames-1 and purely *ab initio* CCSD(T)/aug-cc-pVQZ dipole moment surface (DMS), we have computed Infrared line lists for five symmetric isotopologues of sulfur dioxide: $^{32}\text{S}^{16}\text{O}_2$ (626), $^{33}\text{S}^{16}\text{O}_2$ (636), $^{34}\text{S}^{16}\text{O}_2$ (646), $^{36}\text{S}^{16}\text{O}_2$ (666), and $^{32}\text{S}^{18}\text{O}_2$ (828). The line lists are based on $J=0-80$ rovibrational variational calculations with $E' \leq 8000 \text{ cm}^{-1}$. The $^{34}\text{S}^{16}\text{O}_2$ and $^{33}\text{S}^{16}\text{O}_2$ line lists are compared to the experiment-based models in the High-resolution TRANsmission molecular absorption database (HITRAN2012, <http://www.cfa.harvard.edu/hitran/>) and the Cologne Database for Molecular Spectroscopy, CDMS (<http://www.astro.uni-koeln.de/cdms/>). The accuracy for computed 646 band origins is similar to what has been reported for the main isotopologue, i.e. $0.01 - 0.03 \text{ cm}^{-1}$ for bands up to 5500 cm^{-1} . For rovibrational transitions, the 646 line position and intensity deviation patterns are much simpler and more self-consistent than those of the main isotopologue 626. The discrepancies are mainly found for higher K_a/J transitions. 626 and 646 exhibit comparable line position and intensity agreement for lower K_a/J transitions. The line position deviations for the 636 purely rotational band are parallel to those of 626 and 646, while its line intensity deviations do not show branching patterns as we found in the 626 and 646 cases. Predictions for the other minor isotopologues are expected to exhibit similar accuracy. These line lists are accurate enough to provide alternatives for missing bands of 626 and the minor isotopologues. It may significantly facilitate the laboratory spectroscopic measurement and analysis, as well as to identify these isotopologues in various astrophysical environments.

I. Introduction

Available high resolution spectroscopic data has been quite limited for Sulfur Dioxide (SO_2) in existing databases. For example, the HITRAN (HI-resolution TRANsmission molecular absorption database)[1] includes only seven discrete segments of spectral data for the main isotopologue $^{32}\text{S}^{16}\text{O}_2$ and even less for the most abundant minor isotopologue $^{34}\text{S}^{16}\text{O}_2$. These incomplete data are not suitable for higher temperature (e.g. above 500K) simulations. Since 2009, new experimental analyses from the Ulenikov group [2,3,4,5,6,7,8] have reported a few new vibrational bands up to 5500 cm^{-1} but it is still far from complete. In 2013, Ulenikov et al. [7] also reported a more reliable H_{eff} model for the $^{32}\text{S}^{16}\text{O}_2$ ground state by including the latest experimental information for $34 \geq K_a \geq 29$ transitions. For the other minor isotopologues, only CDMS (Cologne Database of Molecular Spectroscopy) [9] contains some purely rotational band data in the microwave region. Considering the isotopic abundances of $^{32/33/34/36}\text{S}$, the spectroscopic contributions from the other isotopologues may be important in natural SO_2 detection and analysis. Hence, the analysis of astronomical and atmospheric observations indicate a great need for complete and accurate infrared (IR) line lists for the minor SO_2 isotopologues.

Recently we published an empirically refined potential energy surface (PES) for $^{32}\text{S}^{16}\text{O}_2$ using selected HITRAN data with criteria i_{err} (uncertainty index) equal to or higher than 4.[10] The empirical refinement was carried out with the “Best Theory + High Resolution Experiment” strategy, which has been successfully applied before on H_2O , [11] NH_3 , [12,13,14] and CO_2 . [15,16] Compared to the $^{32}\text{S}^{16}\text{O}_2$ data in HITRAN, the σ_{RMS} error for all $J=0-80$ rovibrational energy levels computed on the refined PES (denoted Ames-1) is 0.013 cm^{-1} . Combined with a CCSD(T)/aug-cc-pV(Q+d)Z dipole moment surface (DMS), an IR line list at 296K (denoted Ames-296K) has been computed with $E' \leq 8,000\text{ cm}^{-1}$ cutoff. Compared to the experiment-based models in HITRAN and CDMS, the intensity agreement for most transitions is better than 85-90%. In the higher wavenumber range or higher K_a , the accuracy and agreement degrades slowly and systematically. The Ames-1 PES refinement did not include any recent experimental measurements after 2008, but the accuracy and reliability of the Ames-296K line list predictions have been confirmed several times. All main features in the newly recorded spectra [2-8] by Ulenikov and coworkers match our predictions to within $\pm 0.02\text{ cm}^{-1}$ and $\pm 10\%$, for line position and intensity, respectively. Furthermore, the discrepancies for $K_a > 30$ levels have been solved by comparing to the updated H_{eff} model [7] which included higher K_a experimental data. And our computations suggest that the updated H_{eff} may start losing accuracy beyond $K_a=43-45$.

Such agreement between Ames-296K predictions and experiments clearly indicates that the Ames-1 PES and DMS are reliable enough to provide reliable predictions and alternatives for missing bands and for line lists of isotopologues. This paper presents new Ames-296K IR line lists determined for $^{33/34/36}\text{SO}_2$ and $^{32}\text{S}^{18}\text{O}_2$ and computed using the same Ames-1 PES and the purely *ab initio* DMS. An improved list for $^{32}\text{S}^{16}\text{O}_2$ is also released together. The following section reviews the technical details of the empirical refinement and variational rovibrational calculations. In the Results and Discussion, figures and statistics are presented for the new line lists, plus comparisons between the $^{34/33}\text{S}^{16}\text{O}_2$ lists and HITRAN or CDMS data. A summary and future work are given in last section

II. Technical Details

Most details of the Ames-1 PES empirical refinement and published Ames-296K list for the main isotopologue $^{32}\text{S}^{16}\text{O}_2$ were reported in Ref.10, and full details are not repeated here. In short, a series of *ab initio* energies was fit as a sum of long-range terms and short-range terms, i.e. V_{Short} and V_{Long} .

$$V = V_{\text{Short}} + V_{\text{Long}},$$

where the V_{long} includes Morse-potential terms and part of the quadratic/quartic terms of $\angle\text{OSO}$ bending; the V_{short} includes permutation invariant expansion terms of Δr and $\Delta\cos(\angle\text{OSO})$ which are damped out at the dissociation limit or for strongly

bent structures. The CCSD(T)/cc-pVQZ-DK based PES was chosen for empirical refinement because the $J=0$ band origins for this PES yield the best overall agreement with previous model, probably due to best error cancellations. The fitting root-mean-square error (σ_{rms}) for the 393 *ab initio* energy points below 30,000 cm^{-1} is 0.31 cm^{-1} . Then 5/43/183/158/57 $^{32}\text{S}^{16}\text{O}_2$ HITRAN levels ($ierr \geq 4$ for related transitions) at $J=0/4/20/50/70$, were included in the empirical refinement with 2.5/1.0/1.5/2.0/3.0 weights, respectively. In the end, the weighted σ_{RMS} error was reduced to 0.024 cm^{-1} , and the unweighted σ_{RMS} was reduced to 0.010 cm^{-1} . This refined PES is denoted Ames-1.

It should be noted that an internal parameter adopted in our variational rovibrational program (VTET) [11,17] was not set to a completely converged value, in both pre- and post-refinement computations. Because the parameter only affects the potential part of the matrix elements, not the basis functions, the empirical refinement procedure used in determining the Ames-1 PES essentially corrects the deficiency in the potential expansion. The main consequence is that, it is the effective potential utilized by VTET (using the same parameters as used in the refinement) running with the Ames-1 PES that carries the band origin accuracies reported. That is, other variational programs using the Ames-1 PES will not generate the same band origins unless they use the same procedure as VTET. Certain band origins may have 0.1 – 0.2 cm^{-1} deviations. However, the previously reported band origins and Ames-296K line lists are still accurate to the limits we have quoted (i.e. to $\sigma_{rms} = 0.015 \sim 0.020 \text{ cm}^{-1}$ for rovibrational levels), because these data were generated with VTET calculations using the same parameters as used in the refinement. Thus we expect similar accuracy for the isotopologues presented in this paper as was shown previously for the main isotopologue [10].

The purely *ab initio* dipole moment surface (DMS) was fit from CCSD(T)/aug-cc-pV(Q+d)Z finite-field dipole calculations on nearly three thousand geometries. A much larger number of points is used in fitting the DMS relative to the PES to ensure that regions of the DMS that are changing rapidly are described well. The weighting scheme focused on the region below 30,000 cm^{-1} , for which the average fitting error and average relative error are as small as 1.8×10^{-5} a.u. and 0.010 %, respectively. Such DMS fitting accuracy should be enough to ensure the reliability of intensity predictions on the strongest observable bands up to 6000 cm^{-1} .

Rovibrational energy levels, wave functions, and transition intensity calculations were all carried out with the VTET program as described in Ref.10. We have been using the same energy cutoffs: 0.187 Hartree for solving the one-dimensional stretching Schrödinger equations and later fully contracted basis functions, i.e. 41042 cm^{-1} (1 Hartree = 219,474.6 cm^{-1}); 0.15 Hartree (32921 cm^{-1}) for uncontracted bending functions; 0.12 Hartree (26337 cm^{-1}) for contracted bending functions; 0.06 Hartree (13168 cm^{-1}) for the roots. In addition, a few cases of slowly converging energy levels and intensities have been identified. In order to fix these, we have increased the maximum rotational quantum number from 240 to 360, and the number of quadrature points for the angular part of integrals from 180-200 to 220-240. This is the main improvement for the list of the main isotopologue, 626. These improvements are critical for having a smooth and complete $J=0-80$ based line list at 296K for each isotopologue. The previous $^{32}\text{S}^{16}\text{O}_2$ list excluded the transitions in those slowly converged *JPS* blocks, as mentioned in Ref.10 section D.1. More discussion about potential intensity deviations is presented in section III.5.

III. Results and Discussions

1. Line lists and Isotopic shifts

Table 1 summarizes the number of transitions in each line list reported in this work, plus the zero-point energy (ZPE) and partition functions at 296K for each isotopologue. The ZPEs of 626 and 646 are corrected values as we have found an error in Ref.10 that increased both ZPEs by 6 cm^{-1} . As noted previously [10], a significant number of SO_2 transitions carrying similar intensities. For the CO_2 626 main isotopologue, the 296K.1E-42 complete list ($E' < 24,000 \text{ cm}^{-1}$) has 21 million lines, which is only ~40% of the lines in SO_2 626 1E-36 complete list ($J \leq 80$ and $E' < 8000 \text{ cm}^{-1}$). Consequently, it necessitates keeping ~12% of the transitions in the SO_2 626 1E-36 full list to maintain the 99.9% intensity sum in every 1 cm^{-1} window. In contrast, only

~6% lines were needed during the CO₂ line list size reduction, and there are only ~1 million lines in the similarly reduced 296K.1E-42 lists for CO₂ 626.[16]

[Table 1]

Table 1. Zero-point energy, partition function at 296K, and the number of transitions in the Ames-296K.1E-36 lists and reduced lists (100% abundance). The reduced lists includes all lines with intensity $>10^{-30}$ cm/molecule and maintains $\geq 99.9\%$ intensity sum in every 1 cm⁻¹ spectral window. The degeneracy of 636 nuclei spin is excluded from the partition function value.

# 296K	ZPE (cm ⁻¹)	Partition Function at 296K (J=0-80)	1E-36 List	Reduced List (1E-30 + 99.9%)
626	1529.14	6336.79	50,277,682	6,037,475
646	1514.61	6459.70	51,252,861	6,258,347
636	1521.67	6399.34	55,338,389	6,349,943
666	1501.51	6575.15	52,164,264	6,458,326
828	1470.48	7385.02	58,864,874	7,301,846

2. Comparison of the 626 list to the latest 2014 Experiment

Ulenikov *et al* [8] recently reported the first high-resolution Fourier transform spectra of the weak $\nu_1+\nu_2+\nu_3$ band with $J_{\max}=65$ and $K_{\max}=21$, plus the hot band $\nu_1+\nu_2+\nu_3 \leftarrow \nu_2$ with $J_{\max}=77$ and $K_{\max}=20$. More than 2000 transitions were assigned and 780 rovibrational energy levels were determined. This provides the latest quality check for the published Ames-296K list predictions. Fig.1 (a) shows that most Ames-296K line positions and energy levels agree with experimental values to ± 0.03 cm⁻¹ or better. In Fig.1 (b) and (c), our $\nu_1+\nu_2+\nu_3$ rovibrational level predictions match nicely with the experimentally derived levels to ± 0.05 cm⁻¹. The maximum deviation of energy levels in Fig.1 (b) increases linearly along with the energy. Fig.1 (c) clearly demonstrates the linear correlation between the deviations and J 's, also it shows the deviation does not change much when K_a increases. Obviously, this J -dependence of energy level agreement could be a result of the imperfections in the Ames-1 potential energy terms or the reference geometry.

Absolute Intensities were not directly given in Ulenikov *et al.*[8] so we only compare to the published measurement in the 2999.1 – 3000.0 cm⁻¹ spectral window (see Fig.2). The general agreement is good. For example, the two observed strong transitions, $16_{6,11} \leftarrow 17_{6,12}$ at 2999.43537 cm⁻¹ and $15_{3,12} \leftarrow 16_{3,13}$ at 2999.45520 cm⁻¹, can be found in Ames-296K with -0.00623 cm⁻¹ and -0.00267 cm⁻¹ shifts, respectively. It should be noted that the Ames-296K peak at 2999.71 cm⁻¹ actually includes two transitions: $15_{4,11} \leftarrow 16_{4,12}$ and $16_{7,10} \leftarrow 17_{7,11}$. The observed line positions of the two transitions on the top panel are 2999.70825 cm⁻¹ and 2999.71577 cm⁻¹, separated by 0.00752 cm⁻¹. In our calculations, the two transitions are at 2999.70453 cm⁻¹ and 2999.70851 cm⁻¹, i.e. only 0.00416 cm⁻¹ apart so they blend with each other in the bottom simulation.

On the other hand, the intensity ratios from one strong transition to another do not always agree. For example, the weak $17_{9,8} \leftarrow 18_{9,9}$ peak at 2999.64862 cm⁻¹ in the observed spectra is less than 5% of the strongest peak in the spectral window. But Ames-296K predicts the same transition to possess 37% of the intensity of the strongest peak $15_{0,15} \leftarrow 16_{0,16}$ at 2999.9 cm⁻¹. Such a discrepancy will require further investigation.

[Figure 1]

Fig.1 SO₂ 626 Ames-296K line position accuracy, with respect to the experimental data of the $\nu_1+\nu_2+\nu_3$ band reported in Ulenikov et al, JQSRT 144, 1-10 (2014). [Ref.8].

[Figure 2]

Fig.2 Ames-296K-based ³²S¹⁶O₂ IR simulation (bottom red line) vs. observed $\nu_1+\nu_2+\nu_3$ *P*-branch spectra (top black line, reproduced with permission from Ulenikov et al., J. Quant. Spectrosc. Radiat. Trans. **144**, 1-10 (2014). Copyright 2014 Elsevier Inc.)

3. Comparison of the 646 list to HITRAN2012 / HITRAN2008.

In the HITRAN database, there are 21,382 ³⁴S¹⁶O₂ transitions rising from its $\nu_2=0$ (GS) or the $\nu_2=1$ state, between 0 and 2500 cm⁻¹. The global fit of ³⁴S¹⁶O₂ line positions was carried out by Lafferty, Flaud and co-workers.[18] The intensity data were derived from a CDMS [9] model for a purely rotational band and Flaud, Lafferty and Sams' model [19] for ν_1 , ν_3 and $\nu_1+\nu_3$. By matching J'/J'' and requiring both E'' and $\Delta(E' - E'')$ to match within ± 0.2 cm⁻¹, we have successfully found 21,369 one-to-one matches in the size-reduced Ames-296K.1E-36 list. The 13 remaining lines (unmatched) are high- K_a purely rotational transitions: 6 with $J'=72-73$ and $K_a'=32-34$, plus 7 with $J'=43-48$ and $K_a'=43-44$. As concluded in Ref.10, those very high- K_a extrapolations in HITRAN models could contain usually large uncertainties and can be off by a few tenths of cm⁻¹. Such discrepancies can be corrected by including higher K_a data in the experimental spectra fitting.

[Table 2]

Table 2. Statistical summary for the six ³⁴S¹⁶O₂ bands in HITRAN.

Band in HITRAN	J'_f	K'_a	Freq min	Freq max	No.	Freq Δ_{mean}	Freq $\pm\sigma(\Delta)$	Sum-Int HITRAN*	Sum-Int Dev %	Int δ_{min}	Int δ_{max}	Int δ_{mean}	Int $\pm\sigma(\delta)$	626 Int δ_{mean}	626 Int $\pm\sigma(\delta)$
000 \leftarrow 000	0-80	0-42	0.1	227.8	10604	0.016	0.009	9.656E-20	1.5%	-8.3%	48.0%	6.0%	8.0%	10.1%	11.2%
100 \leftarrow 000	0-64	0-23	1060.2	1231.2	3456	0.010	0.002	1.389E-19	1.3%	-13.2%	2.4%	-1.0%	2.6%	0.7%	11.1%
110 \leftarrow 010	3-46	0-14	1091.5	1195.0	834	-0.006	0.002	6.654E-21	0.7%	-5.1%	1.0%	-0.2%	1.0%	0.3%	17.9%
001 \leftarrow 000	0-74	0-28	1294.4	1384.2	3377	-0.011	0.003	1.118E-18	2.0%	-11.0%	7.9%	-1.6%	3.5%	-3.7%	6.7%
011 \leftarrow 010	0-60	0-22	1301.6	1373.3	1913	-0.016	0.003	8.850E-20	2.0%	-5.2%	3.8%	0.2%	2.2%	-0.3%	6.7%
101 \leftarrow 000	1-51	0-18	2439.3	2500.4	1185	0.018	0.006	2.114E-20	10.3%	-19.8%	-4.0%	-10.8%	2.6%	-11.0%	5.2%

* 646 abundance 0.04195 is included in intensity comparison.

[Figure 3]

Fig. 3 Agreement and discrepancy on the SO₂ 646 purely rotational transition position and intensity: Ames-296K vs. HITRAN.

[Figure 4]

Fig.4 Ames-296K line list for the SO₂ 646 isotopologue compared to HITRAN data: line position and intensity deviations vs. $K'_a'+J'/100$.

An interesting comparison is to examine the Ames-296K line position and intensity deviations plotted side by side for the 626 and 646 bands in HITRAN. Detailed comparison of 626 line position and line intensities between Ames-296K and HITRAN2012 models have been given in the file “13_HITRAN_bands.pdf” included in the supplementary material for Ref.10 [20]. To save paper and trees, interested readers please download the file and do their own comparison. The agreement for the 646 purely rotational transitions is shown in Fig.3, while the agreement for other bands is shown in Fig.4. In Fig.4, both absolute values and distribution range of the line position and intensity deviations are significantly reduced, even in the same J/K_a range. The patterns for a fundamental band ν_1 (or ν_3) and the corresponding hot band $\nu_1+\nu_2\leftarrow\nu_2$ (or $\nu_2+\nu_3\leftarrow\nu_2$) are more

consistent.

In Fig.4 (a), both line position and intensity deviations for ν_3 are consistent with the 626 results but are distributed in a narrower range: $-0.015 - 0.00 \text{ cm}^{-1}$ and $-10\sim 5\%$. The deviation pattern for the $\nu_2+\nu_3 \leftarrow \nu_2$ hot-band shown in Fig.4 (e) is very consistent with those for ν_3 , but not quite as consistent with that for 626 $\nu_2+\nu_3 \leftarrow \nu_2$. The highest J/K_a are 80/33 (626) vs. 74/28 (646) for ν_3 , and 70/25 (626) vs. 60/22 (646) for $\nu_2+\nu_3 \leftarrow \nu_2$.

In Fig.4 (b), the ν_1 line position deviations are between 0.00 and 0.02 cm^{-1} , vs. the $-0.03 \text{ cm}^{-1} - 0.02 \text{ cm}^{-1}$ range for 626. Relative intensity deviations are between -10% and 0% , which is much smaller than the 626 range: $-35\% \sim 20\%$. Compared to 626, the 646 ν_1 deviation pattern of line positions is similar but the intensity deviation pattern is much simpler. A similar pattern is found for the related hot-band $\nu_1+\nu_2 \leftarrow \nu_2$. The highest J'/K_a' are 80/32 (626) vs. 64/23 (646) for ν_1 , and 45/21 (626) vs. 46/14 (646) for $\nu_1+\nu_2 \leftarrow \nu_2$.

The $\nu_1+\nu_3$ band in Fig.4 (c) has a small positive K_a dependence for intensity deviations, which is opposite to that for 626. This is interesting as it is the only such pattern found in the six comparable HITRAN bands. Note the highest J/K_a are 80/24 (626) vs. 51/18 (646). The 626 line position deviations exhibit a dramatic change beyond $K_a=18$, where no data or model is available for 646.

Based on the 626 vs. 646 comparisons, we are inclined to suggest the 646 data models in HITRAN2012 are less extrapolated so they are overall more self-consistent and reliable. The extrapolations can be less in either J/K_a or ΔK_a . This paper is mainly to report both agreement and discrepancies while more detailed analysis will be carried out later. We hope future high resolution 646 spectral measurements can help identify the source behind those discrepancies.

4. Comparison of the $^{33}\text{S}^{16}\text{O}_2$ list to the CDMS model.

For 636, CDMS provides a purely rotational band model with hyperfine splitting. No vibrational bands are available in either HITRAN or CDMS. The model was fit from 585 experimentally measured lines with $J'=1-43$ and $K_a'=1-10$. The experimental line positions were taken from Refs.[21,22,23]. These experimental lines were split from 145 regular transitions due to nuclei spin rotation couplings, as ^{33}S has a spin of $5/2$. The fitted model was utilized to derive 19,067 CDMS lines which can be summed into 4136 pre-splitting transitions, with $J'=1-82$ and $K_a'=1-31$.

In order to compare the Ames-296K transitions (no hyperfine structure available) with the CDMS transitions, Ames-296K intensities need to be converted to 300K. Our partition function values at 300K and 296K are 6552.06 and 6399.34, respectively. The line position variations in a given spin-rotation split structure usually are less than 0.0005 cm^{-1} , so the numerically averaged line position should be a reliable value with which to compare. The intensity distribution pattern within a split structure is beyond the scope of our calculations, while the simple sum of intensities in a split structure is found comparable to the Ames intensity prediction. This is how we compute the Ames vs. CDMS line position deviations (in cm^{-1}) and the relative intensity deviation (in %). The results are reported in Fig.5.

[Figure 5]

Fig.5. $^{33}\text{S}^{16}\text{O}_2$ line position and relative intensity deviations: Ames-296K vs. CDMS. The Ames-296K intensities are converted to 300K and compared to the sum of intensities in each hyperfine structure. Each hyperfine structure is treated as “one” line. Ames line positions are compared to the numerically averaged CDMS line positions in each hyperfine structure. (a) comparison to the 145 experimentally measured lines; (b) comparison to all 4136 lines in CDMS.

In Fig.5 (a), Ames line positions match the majority of the experimental measurements with better than 0.001 cm^{-1} agreement, but a few Ames line positions at $K_a=2-4$ are higher by $0.001 - 0.004 \text{ cm}^{-1}$. Most Ames intensity predictions have $-5\% \sim -10\%$ deviations. For 626 and 646, the Ames intensity predictions are usually within 1–3% of CDMS values. Further

investigation is required in order to identify the source of this systematic discrepancy. One transition $J_{Ka,Kc} = 16_{2,14} \leftarrow 17_{1,17}$ is not shown in Fig.5 (a) because there were only 2 measured lines: $F=15 \leftarrow 16$ and $F=18 \leftarrow 19$. Their intensity sum is $1.436\text{E-}25$ cm/molecule, while the Ames intensity is $2.647\text{E-}25$ cm/molecule. The relative intensity deviation is 65.1%, i.e. out of the plot range.

Fig.5 (b) compares to the full CDMS model-based line set. It shows a line position deviation pattern very similar to those we found for 626 and 646.[10] The tail feature at higher $K_a > 25$ probably results from the extrapolation error due to limited experimental data $K_a \leq 10$. The agreement can be improved by including higher K_a experimental information in the fits. The line position deviations at lower K_a + higher J may come from the deficiency of the Ames-1 PES refinement during which the purely rotational band data had same weights as higher energy rovibrational data. We expect these deviations to be significantly reduced in a future Ames-2 PES refinement.

On the other hand, the 636 purely rotational band intensity agreement between Ames and the full CDMS are obviously better than those of 626 and 646. In Fig.5 (b), most relative intensity deviations are in the range from -10% to 0%. The positive K_a -dependence is similar to that found for the lowest branch of the 646 comparisons depicted in Fig.3 (b). We are inclined to believe these K_a dependences result from a possible deficiency in our dipole model or wavefunction calculations. Compared to Fig.3 (b), the better agreement at the lower K_a end could be due to less extrapolation in the CDMS model. For example, the upper branch in Fig.3 (b) cannot be found in Fig.5 (b) and the higher J extrapolations at lower K_a do not exist, either. Our Ames-296K line lists are presumably of the same quality and consistent for all isotopologues.

Note that in Fig.5 (b), there are two groups of intensity outliers where Ames predictions carry $\sim +30\%$ or $\sim +70\%$ deviations. These are probably the incomplete hyperfine split structures in CDMS in which at least one or two strong transitions are missing.

Currently no data is available for the 666 or 828 isotopologues in HITRAN or CDMS. The Ames-296K line lists for 666 and 828 and other 636 bands are expected to have similar line position and intensity accuracy for most low J or low K_a transitions. For the high K_a and high ΔK_a transitions on which we found larger intensity discrepancies in the 626 and 646 isotopologues, the accuracy may depend on the degree of spectral model extrapolations, as well as the convergence of our rovibrational variational calculations.

IV. Summary and Future work

Using the same empirically refined Ames-1 PES, *ab initio* DMS, and the same or improved rovibrational calculation parameters, we have computed Ames-296K line lists for five symmetric isotopologues of SO₂. These lists are compared with the available spectral models in HITRAN and CDMS (including the experimental dataset from which they were fit). The agreement and deviations for line positions and intensities are discussed and compared to those of the main isotopologue, 626. It is concluded that the Ames-296K predictions are reliable and accurate enough to provide alternatives for spectral regions where no experimental data or models are available. It is also capable of helping experimentalists assign those weaker bands or isotopologue transitions. It is suggested the agreements at higher J/K_a levels between Ames-296K and the databases may rely on how far the spectral models have been extrapolated. We sincerely hope the lists can facilitate the observation and analysis of SO₂ high-resolution IR spectra, especially those higher energy or weaker intensity bands. We expect to incorporate them into our future PES refinements. In this way, we can push the SO₂ spectral data to a larger range and higher standards.

It should be noted the applicable T range of the current Ames-296K line lists are from 0 up to 500K. Both the original and size-reduced line lists should use caution in $T > 500\text{K}$ circumstances. This applies to all five isotopologues. We choose to report the original $1\text{E-}36$ cm.molecule⁻¹ line lists while noting that the known contamination and defects in weaker lines will rise along with temperature. This is because the main motivation here is to provide reliable enough reference data to facilitate the experimental data analysis. But purifying the lists up to high temperatures (e.g. 1000K) will either require a larger amount

of highly accurate experimental data (including intensities) or will require significantly more tests of the rovibrational calculations (including intensities) in order to eliminate very small errors. The next step is to compute Ames-296K lists for asymmetric isotopologues, including 628, 627 and 648, 637 etc. In the mean time, we are preparing to carry out the next cycle of PES refinement (Ames-2) and line list purifications.

The line lists exceed the supplementary file size limit. All five Ames-296K line lists are available upon request. The size-reduced line lists can be downloaded from <http://huang.seti.org/>.

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